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## PHOTON ECHO STIMULATED FROM OPTICALLY INDUCED NUCLEAR SPIN POLARIZATION

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A new type photon-echo is reported which is stimulated from optically induced nuclear spin polarization in the electronic ground state of a molecular radical. The echo was observed in the  $^2A_1 \leftarrow ^2A_1$  electronic transition at 514.2 nm of triphenylmethyl in triphenylamine at 1.5 K. Evidence is also presented that *intra*-molecular spin cross-relaxation processes determine the relaxation of the normal stimulated photon echo in triphenylmethyl at low temperature.

Recently a number of new spin [1] and optical [2] echo phenomena have been reported which are peculiar to multilevel systems. We mention here the tri-level spin echo detected in Al [3], the Raman echo [4] observed in CdS [5], and the tri-level photon [6,7] and two-photon [8] echo generated in Na vapour.

A prerequisite to observation of these echoes is that at least one level (virtual in the Raman echo case) is optically connected to two other levels in the level structure that participates in the echo formation. When the multilevel structure, which participates in the photon echo formation, is due to hyperfine splitting, optical branching is known to cause modulation of the echo intensity versus pulse delay [9,10].

In this letter we will show that from such a level structure also a new type anomalous [6] stimulated photon echo (3PSE) may be generated whose origin is closely related to that of the afore-mentioned ones. The interesting *new* feature of this photon echo is that its lifetime *solely* depends on the lifetime of the hyperfine levels in the ground state.

We demonstrate the existence of such an echo on the organic mixed crystal system triphenylmethyl (TPM) in triphenylamine (TPA) but emphasize that such an echo should also be observable in systems as ruby [9],  $\text{Pr}^{3+}$  in  $\text{LaF}_3$  [10] and Na vapour [7,8]. The anomalous 3PSE was observed on the 514.21 nm  $^2A_1 \leftarrow ^2A_1$  electronic transition of TPM as a guest (ca.  $10^{-3}$  mol %) in TPA at 1.5 K.

The experimental set-up, used to generate the 3PSE

was very similar to the one recently described by Morsink et al. [11]. Briefly, two nitrogen lasers, an AVCO C-950 and a Molelectron UV-400 which could be independently triggered, were used to pump two dye-lasers of the Hänsch design [12]. Both dye-lasers produced 5 ns pulses with a spectral width of  $0.5 \text{ cm}^{-1}$ . As lasing dye we used 7-dimethylamino-4-trifluoromethylcoumarin (Exciton dye Coumarin 485), at a concentration of  $10^{-2} \text{ mol/l}$  in ethanol. As for a stimulated photon echo three pulses are needed, the output pulse of one dye-laser was split and one part sent through an optical delay line. All three optical pulses were then recombined using suitably positioned beam-splitters. In the experiment to be discussed the time separation between the first two excitation pulses was fixed at 40 ns, while the probe (third) pulse delay was under electronic control and varied between 60 ns and 5 ms. The 3PSE was detected with a photomultiplier (type RCA-7265) which was protected, from saturation by the collinear exciting pulses, by an optical shutter-gate system [11] that tracked the imposed delay of the third excitation pulse. The magnetic field was supplied by a superconducting magnet obtained from the British Oxygen Company. For further details on the set-up consult ref. [11]. The mixed crystals of TPM in TPA were prepared as previously described by Hesselink and Wiersma [13]. In the 1 mm thick crystal used in the experiments about 30% absorption was obtained.

We now proceed by discussing the results of the

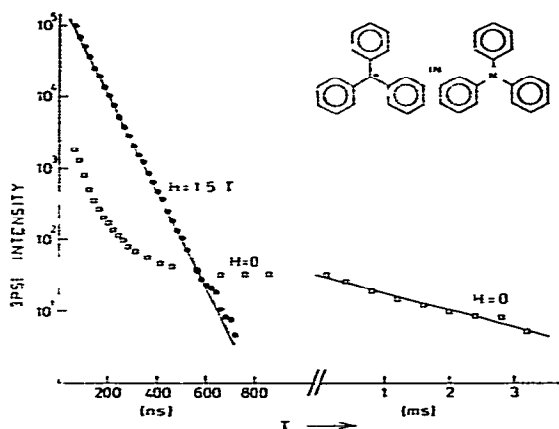


Fig. 1. Intensity of the stimulated photon echo of triphenylmethyl in triphenylamine at 1.5 K versus second-third pulse delay in zero field and in a magnetic field of 1.5 T. The time separation between the first and second pulse was 40 ns.

3PSE experiment which are shown in fig. 1. We first note that in zero magnetic field the stimulated photon echo clearly exhibits two different decay channels. The first channel in the decay of the 3PSE has previously [13] been interpreted as due to the decay of the population at the optical frequency. The non-exponential nature of this decay was thought to arise from cross-relaxation in the manifold of electron-nuclear spin states. Proof for this supposition has now been obtained from a 3PSE study of the completely deuterated TPM radical. For this species the initial decay of the 3PSE in zero field up to 400 ns, is completely exponential, with a lifetime of half the fluorescence lifetime (160 ns), while a magnetic field no longer affects the 3PSE intensity. This shows that the spin diffusion processes, on this time scale, have been frozen out.

We note here that this experiment shows that in TPM the *intra*-molecular spin-diffusion processes dominate the echo decay behaviour. This is an interesting fact to consider in the present discussion [14] on the question whether or not an intramolecular heat bath can induce optical dephasing different from the (trivial) fluorescence decay.

Returning now to fig. 1, one observes that in a high magnetic field (1.5 T), the second decay channel of the 3PSE vanishes, while the first one leads to purely

exponential decay over more than four decades of intensity change. This purely exponential decay of the 3PSE in a high magnetic field may be understood [13] by realizing that in a high magnetic field, optical branching no longer occurs (the electron and nuclear spin are quantized along the magnetic field). This implies that the hyperfine splitting in the ground and excited state to the radiation field merely looks as a source of inhomogeneous broadening. This experiment therefore conclusively shows that the second decay channel (anomalous 3PSE!) is only available in case of optical branching. The lifetime of this anomalous photon echo ( $1.9 \pm 0.1$  ms), which is very long compared to the fluorescence lifetime (131 ns), strongly suggests that only ground state levels play a role in the decay. We also note that, upon deuteration of the molecule, the lifetime of the anomalous 3PSE increases by a factor of 2, which supports the idea that spin-relaxation processes determine the echo decay. We therefore conclude that the anomalous 3PSE in TPM arises from spin alignment in the ground state prepared by the first two excitation pulses.

In order to confirm this idea and to obtain a more clear physical picture of the anomalous 3PSE formation we have performed calculations on the simplest model system that has all the important features of the TPM radical. Fig. 2a shows that we approximate the very complex level structure appropriate to TPM (there are 65536 hyperfine levels in both the ground and excited state!) by a simple three level model system. For this system we have calculated the effect of a three pulse sequence, shown in fig. 2b, on the polarization at the optical frequencies  $\nu_{32} = (E_3 - E_2)/\hbar$  and  $\nu_{31}$  at the time  $t = t_1 + 3\Delta t + T + t_2$ . The following density matrix equation was solved [15]:

$$\dot{\rho}(t) = (i\hbar)^{-1} [\mathcal{H}, \rho] - \frac{1}{2} \{\Gamma, \rho\} + F,$$

where  $\rho$  is the single molecule density matrix,  $\mathcal{H}$  the hamiltonian of the system including the radiation field,  $\Gamma$  the decay matrix and  $F$  the feeding matrix.

These matrices for our system take the following form:

$$\Gamma = \begin{pmatrix} W_{12} & 0 & 0 \\ 0 & \Gamma_{21} & 0 \\ 0 & 0 & \Gamma_{31} + \Gamma_{32} \end{pmatrix}$$

and

$$F = \begin{pmatrix} \Gamma_{31}\rho_{33} + \Gamma_{21}\rho_{22} & 0 & 0 \\ 0 & \Gamma_{32}\rho_{33} + W_{12}\rho_{11} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

$\Gamma_{32}$  and  $\Gamma_{31}$  are the optical relaxation rates (radiative and radiationless) of the upper level into the lower ones.  $\Gamma_{21}$  and  $W_{12}$  are the spin relaxation rates among the hyperfine levels in the ground state. We note here that our calculation extends the work of Schenzle et al. [16] on a three level system and that our results, for infinite relaxation times, for a two-pulse sequence are in agreement with theirs.

In our calculation we assume that  $T \gg \Gamma_{31}^{-1}, \Gamma_{32}^{-1}$  which implies that at time  $t = t_1 + 2\Delta t + T$ , the elements of the density matrix  $\rho_{13}, \rho_{31}, \rho_{23}, \rho_{32}$  and  $\rho_{33}$  for all practical purposes equal zero. The calculations which followed the procedure suggested by Brewer [17] show that indeed at  $t = 2t_1 + 3\Delta t + T$  an optical echo may be expected whose decay, as a function of  $T$ , is only determined by relaxation among the lower levels. Details of this calculation will be published elsewhere.

The physical picture for the anomalous 3PSE formation that emerges from the calculations is the fol-

lowing. The first two excitation pulses at time  $t = t_1 + 2\Delta t$  create within the inhomogeneous optical lineshape a frequency dependent optical polarization. Such a polarization grating is known to yield the normal (two pulse) photon echo. Simultaneously however at  $t = t_1 + 2\Delta t$  the first two excitation pulses create also a *frequency dependent spin polarization* in the electronic ground state. The important point to note here is that there exists a one to one correspondence between the optical and spin polarization in any molecule of the ensemble. While the optical polarization decays fast (not slower than  $\frac{1}{2}(\Gamma_{31}^{-1} + \Gamma_{32}^{-1})$ ) the spin polarization in the electronic ground state decays slowly through spin-lattice relaxation. The anomalous 3PSE now is formed when a third excitation pulse comes along at a time  $t = t_1 + T + 2\Delta t$  such, that all optical polarization is lost while significant spin polarization is still present. The third excitation pulse excites from this frequency dependent spin polarization a frequency dependent polarization at the optical frequency which mimics the situation present at  $t = t_1 + 2\Delta t$ . At time  $t = 2t_1 + 3\Delta t + T$  we therefore expect the formation of an optical echo, which we name the anomalous 3PSE. We note that the physical picture of the echo formation described here is reminiscent to the description of polarization echoes in piezoelectric powders [18]. In the above tri-level system the anomalous 3PSE in the time  $T$ , only decays through spin-lattice relaxation among the hyperfine levels in the ground state. In a real multilevel system, cross-relaxation also destroys the original nuclear spin polarization. We therefore expect that in a system where there are only a few hyperfine levels, the echo lifetime would become much longer. This is a point of further investigation.

In summary, we have observed an anomalous photon echo which is stimulated from optically induced nuclear spin alignment in the electronic ground state of a molecular radical. This echo is expected to be observable in many systems whose multilevel nature is due to hyperfine splitting. The echo may possibly be used as an additional probe for the study of spin relaxation processes at zero field in the electronic ground state. In addition we have shown that the decay of the normal stimulated photon echo is affected by *intra*-molecular spin relaxation processes. This implies that in an *isolated* TPM molecule optical dephasing may occur by intramolecular relaxation.

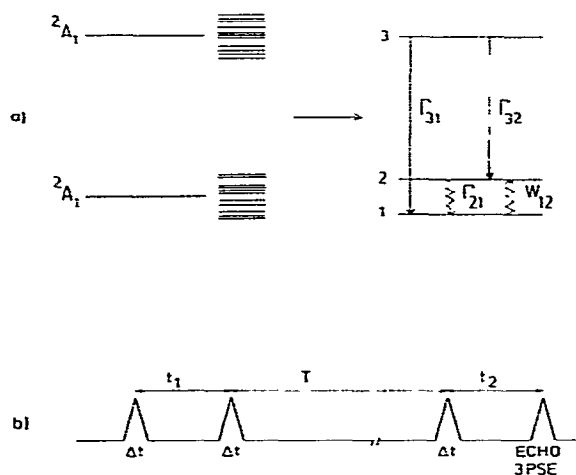


Fig. 2. (a) Model-level systems for triphenylmethyl. Levels 1 and 2 are hyperfine levels of the electronic ground state while level 3 is one of the hyperfine levels in the electronically excited state. (b) Optical pulse sequence used to generate the stimulated photon echo.

### Note added

We have recently been able to observe a stimulated photon echo with a lifetime of 30 minutes in the  $^3P_0 \leftarrow ^3H_4$  transition of  $Pr^{3+}$  in  $LaF_3$  [19]. This finding confirms the analysis of the anomalous photon echo formation as described in this paper.

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